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Department of Physics and Astronomy
Delaware State College
Dover, Delaware 19901

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CROSS-SECTION AND THRESHOLD ENERGY OF
NEGATIVE IONS IN CARBON DIOXIDE
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PROGRESS REPORT

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The Photodetachment Cross-Section and Threshold
Energy of Negative Ions in Carbon Dioxide Funded
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submitted by

Dr. Ehsan M. Helmy
Principal Investigator
Physics Department
Delaware State College
Dover, Delaware 19901
302-678-5158

and

Dr. S.B. Woo
Co-principal Investigator
Physics Department
University of Delaware
Newark, Delaware 19711
302-738-2671

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A. PRELIMINARY RESULTS

Under Section (A) we give a summary of preliminary results and our interpretation of these results. A very brief description of how the results are obtained is also given.

I. Recent publications on Photodetachment of CO_3^- :

Since the submission of our proposal the following reports became available:

1. Threshold energy and sunlight photodetachment rate for CO_3^- and $\text{CO}_3^-\cdot\text{H}_2\text{O}$ were reported by Burt¹ and shown in the table below.

Threshold energies and solar photodetachment rates.

Ion	Photodetachment threshold energy	Sunlight photodetachment rate	Reference
O^-	1.46 eV	1.44 sec^{-1}	Branscomb
CO_3^-	1.8(0.2) eV	1.4(30%) sec^{-1}	Burt
$\text{CO}_3^-\cdot\text{H}_2\text{O}$	2.1(0.2) eV	1.1(30%) sec^{-1}	Burt

He also reported a photodetachment cross section for CO_3^- shown in Fig. 1.

The apparatus and technique used by Burt embody the idea of photodetachment-in-drift-tubes. But there is one significant difference. Instead of detecting photodetached electrons as we do, he de-

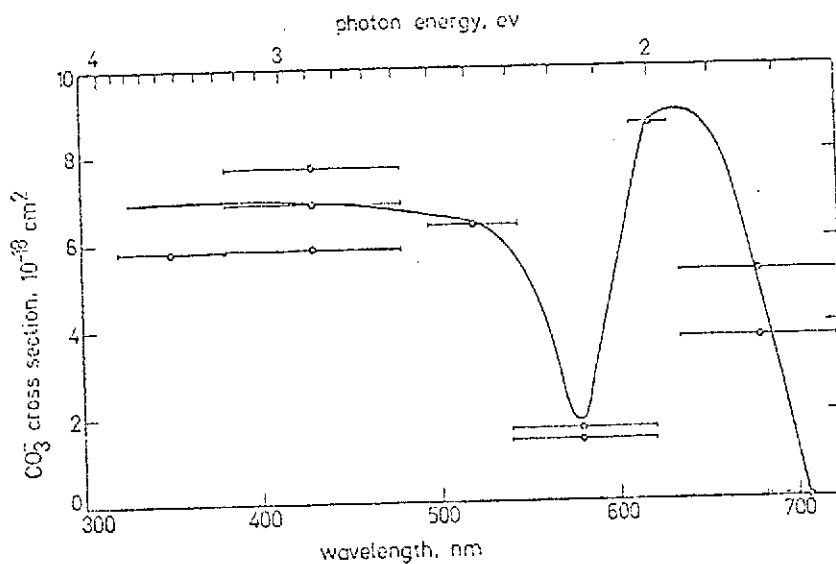


Fig. 1. Photodetachment cross section vs wavelength for CO₃⁻. The circles are data from a typical run. Reproducibility \pm 30%. The solid curve is the assumed smoothed cross section. The Error bars show the effective bandpass of the filter combinations.

J.A.Burt, J.Chem. Phys. 57, 4649 (1972)

tests the attenuation of CO_3^- ions after their interaction with the photon beam. This, among other things, subjects him to the danger of not being able to distinguish between photodetachment of CO_3^- and photodissociation of CO_3^- . The following remarks about his results are worth noting.

2. Ferguson, Fehsenfeld and Phelps² commented on Burt's publication. They pointed out that the threshold energy of CO_3^- should be larger than 2.9 ($\pm 0.3\text{eV}$) using data from previously established thermochemistry. They suggested that Burt might have observed the photodissociation of CO_3^- for which the threshold energy would be $D(\text{CO}_2-\text{O}^-) \approx 2.2\text{eV}$ which is within the range of Burt's 1.8eV.
3. Burt replied³ saying that Ferguson et al's calculation was based on the known exothermicity of $\text{O}_3^- + \text{CO}_2 \rightarrow \text{CO}_3^- + \text{O}_2$ reaction. But two forms of CO_3^- may be possible: $(\text{O}=\text{C}-\text{O}-\text{O})^-$ and $(\text{O}=\overset{\text{O}}{\underset{\cdot\cdot}{\text{C}}}-\text{O})^-$. An alternate route of formation of CO_3^- such as $\text{O}^- + \text{CO}_2 + \text{M} \rightarrow \text{CO}_3^- + \text{M}$ may produce a higher (lower electron affinity) isomeric form. Burt did not say but seemingly implied that his CO_3^- was produced that way.

II. Our Preliminary Results:

Using basically the same apparatus and technique as described in reference four, we find that the lamp

light (i.e. entire photon spectrum of the 2.5 Kwatt high pressure Xe arc lamp - see Fig. 2) photodetachment signal is 211 ± 80 units. The pressure in the drift tube is 1.8 torr and E/p_0 is 5.0v/cm-torr. While keeping all the other variables constant, we find that the signal for color filter CS 3-71 (See Fig. 3) is -35.9 ± 58 ; for CS 7-51 is 58 ± 35 ; for CSO-53 (pyrex) is 140 ± 53 . The reaction which produces CO_3^- ion in our drift tube is $\text{O}^- + 2\text{CO}_2 \longrightarrow \text{CO}_3^- + \text{CO}_2$ (See Section B).

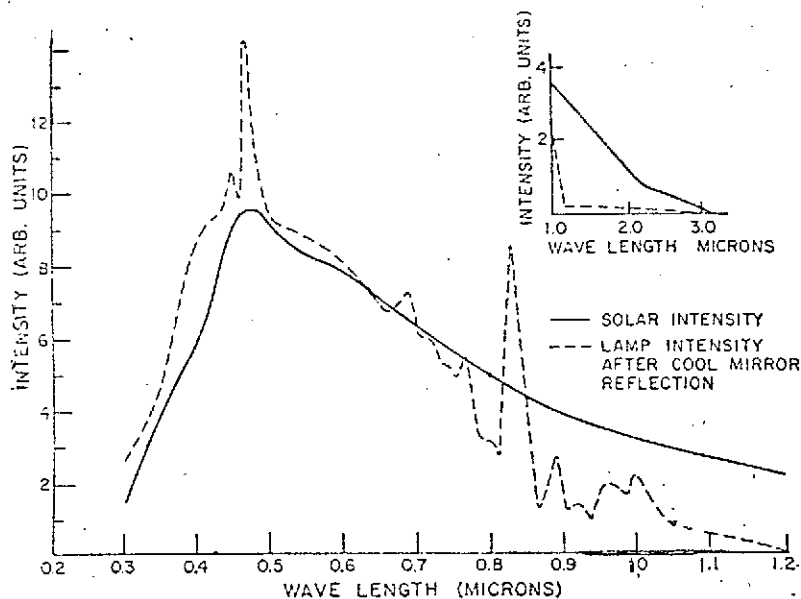


Fig. 2. Comparison of light intensity distribution of the 2.5 kw light pressure Xe lamp with that of the sun.

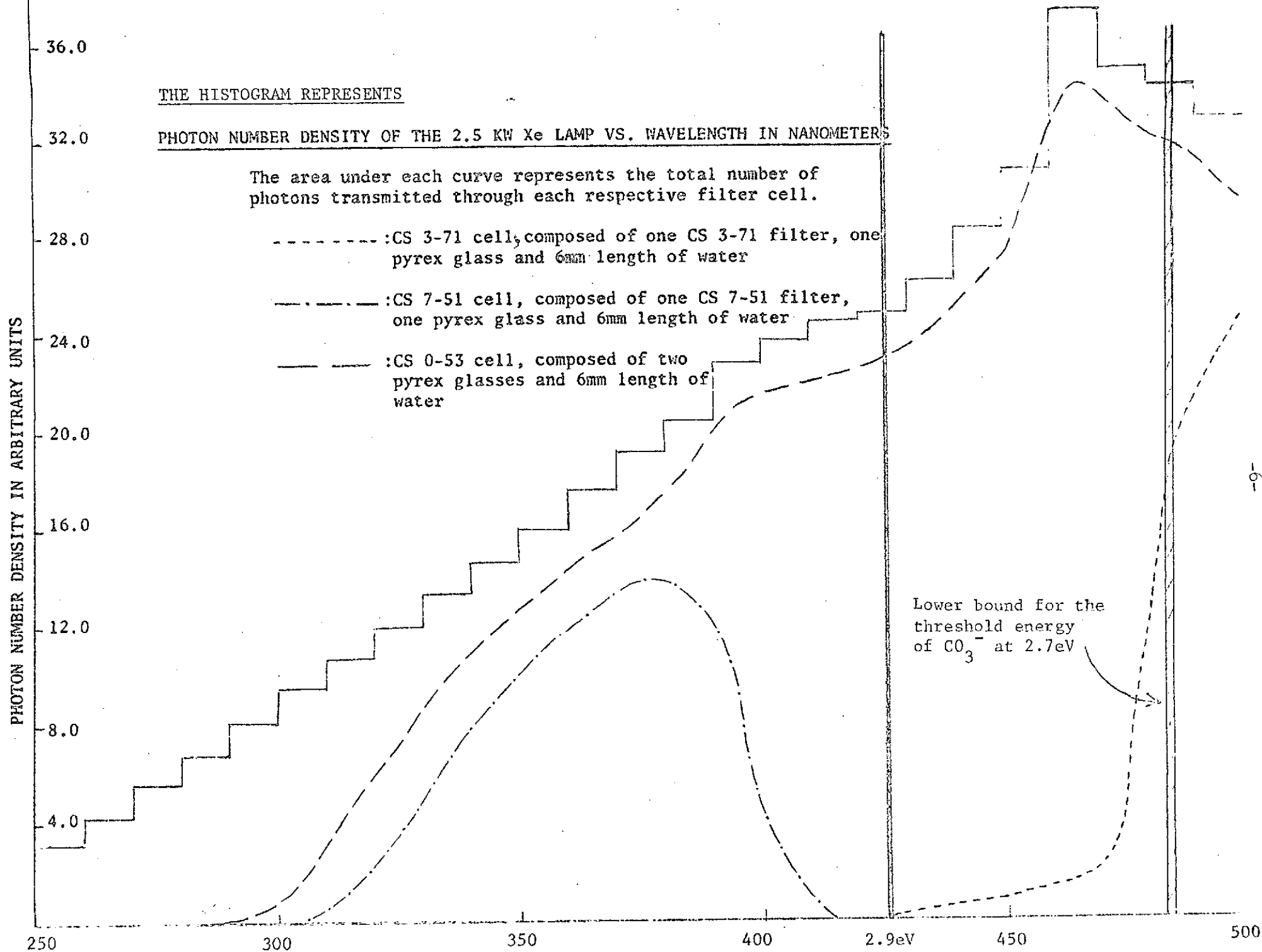


Fig. 3 Wave Length (n.m.)

We interpret our preliminary results to mean the following:

1. The electron affinity of CO_3^- is larger than 2.7eV.
2. Since our CO_3^- is predominantly, if not entirely, produced from the $\text{O}^- + 2\text{CO}_2 \xrightarrow{2} \text{CO}_3^- + \text{CO}_2$ reaction, Burt's conjecture that there is an isomeric form of CO_3^- is likely in error.
3. If one assumes that the threshold energy is at 4250A (i.e. 2.9eV), and draws a straight line there (See Fig. 3) then one will count roughly 40, 80 and 120 units of photons (each unit represented by 1 cm^2) under the curves represented respectively by CS 7-51, CS 0-53 and lamp light. These three numbers correspond surprisingly well with preliminary measured photodetachment signals of 58, 140 and 211. Hence we conjecture that the photodetachment cross section of CO_3^- will roughly be like a step function across the range of 4250 to 2500A, having its threshold energy at 4250A. The above is a conjecture because two of the four data points have unduely large one standard deviation values. To bring these standard deviations down to acceptable values will take at least another 48 hours of integration, which we do not deem appropriate at this stage of the investigation. Eventually many more filters will be introduced. The signal to noise ratio of all data points will achieve a respectable level and least squares fit for the

cross section based on a power series representation expanded about the threshold energy will be done.

4. The sunlight photodetachment rate for CO_3^- is likely to be much smaller than that reported by Burt. Reasonings will not be given in this report, because they will be lengthy and somewhat iffy. However, this is our current best educated guess.
5. In order to put the relative photodetachment cross section measurements on an absolute scale, one must know the attachment coefficient of CO_2 gas. According to Bhalla and Craggs⁵, the probability of having the photodetached electrons re-attach to form negative ions (and thereby evading our electron detector) is much less than 1%. We independently verified that.

B. PRELIMINARY IDENTIFICATION OF CO_3^-

Positive identification of the photodetached ion depends on the completion of the mass-identified drift tube (See Section C). Here we report preliminary identification using supporting evidences gathered in drift tubes.

Using a mass identified drift tube having a continuously operated electron source, Moruzzi and Phelps⁶ reported the relative ion intensity as a function of E/p in CO_2 gas. This is shown in Fig. 4.

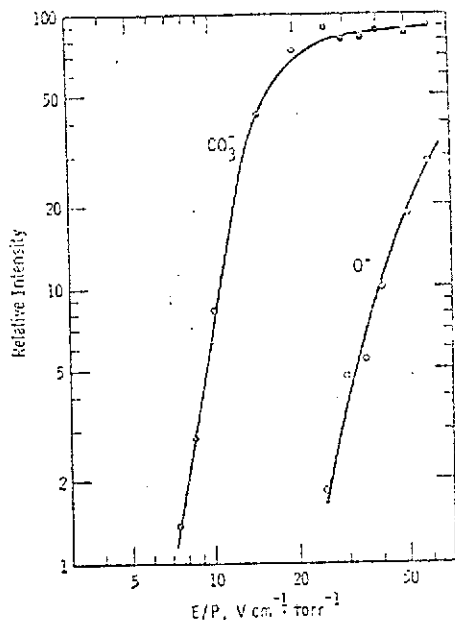


Fig. 4.

The relative ion intensity as a function of E/p in carbon dioxide. No negative ions were detected at low values of E/p . For values of $E/p > 7 \text{ V cm}^{-1} \text{ torr}^{-1}$ dissociative attachment producing O^- is the initial reaction. However this is followed by a rapid three-body conversion process which produces CO_3^- . $p = 1.74 \text{ torr}$.

Moruzzi and Phelps, J.Chem. Phys. 45, 4617 (1966)

Using their data as a guide, we examine the arrival time spectrum gathered from our static drift tube having a pulsed, cold cathode discharge ion source. At compatible combined conditions of p , E/p and drift tube length, we substantially, verify Moruzzi's findings. At those conditions, we see two ion species only.* The ion with higher mobility is the primary ion, presumably O^- produced from $\text{CO}_2 + e \rightarrow \text{CO} + \text{O}^-$. This primary ion converts at a very fast rate forming a slower ion

* A third ion, having an even smaller mobility than CO_3^- , is seen when the dry ice-acetone cold trap is not used. We assume that it is the $\text{CO}_3^- \text{H}_2\text{O}^-$ ion.

species, the conversion rate is found to be p^2 dependent. This is consistent with Moruzzi's finding that the slower ion is CO_3^- , formed through the $\text{O}^- + 2\text{CO}_2 \longrightarrow \text{CO}_3^- + \text{CO}_2$ reaction.

The exact operating conditions for the production of pure CO_3^- in our drift tube will of course be somewhat different from those specified by Fig. 4. Our drift tube has a cold cathode discharge ion source. Its drift space length is about six times longer. Hence, we will obtain pure CO_3^- in the photodetachment region of the drift tube so long as the pressure is larger than 1 torr and the E/p is less than 12 volt/cm.torr.

C. THE CONSTRUCTION OF THE MASS-IDENTIFIED DRIFT TUBE.

The construction of the mass- identified drift tube is in progress. The drift tube itself has been constructed. (Recall that our project calls for two drift tubes. One is where the photodetachment experiment is and will be done. The other which is to be connected to a mass spectrometer will be used for mass identifying the ions, while keeping its operating conditions "identical" to the photodetachment-drift-tube). A stainless steel tee which connects the drift tube to an existing mass spectrometer has been constructed. The ion optics assembly which will be located within the tee for guiding ions from the drift tube to the mass spectrometer is completed. We will shortly be connecting the drift tube to the mass spectrometer to test the gas handling ability of an existing Veeco pump station. The electronics for the new drift tube is about half finished. The electronics for counting the ion pulses coming through the mass spectrometer is about half finished. The following diagrams showing the design specifications of various components are appended.

Fig. A: The drift tube assembly.

Fig. B: Stainless steel tee assembly, having
8" flanges.

Fig. C: The ion optics assembly.

Fig. D: The Supermica plate which isolates the
high voltage drift tube assembly from
the connecting stainless steel hard ware,
which must be at ground.

A schematic diagram of the over-all design of the mass
identified drift tube is shown in Fig. 5.

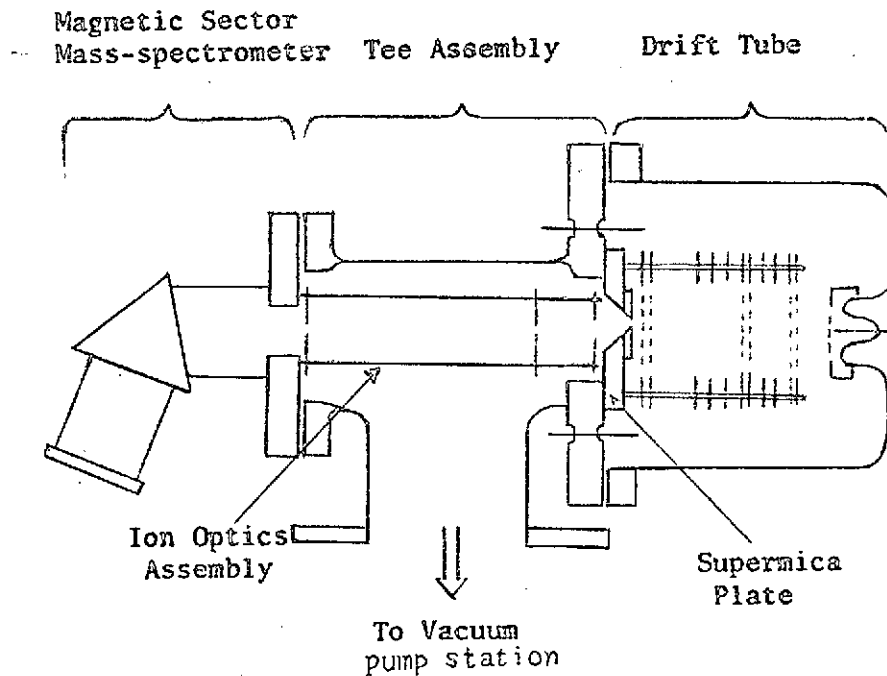


Fig. 5. A schematic diagram of the over-all design
of the mass-identified drift tube.

D. PLANS FOR PHOTODETACHMENT OF CO_4^- :

Our approach to the photodetachment of CO_4^- will be very similar to that reported for CO_3^- . Results of Moruzzi and Phelps will be used as guide lines to locate in our drift tube the best combination of total pressure, ratio of partial pressure of CO_2 to partial pressure of O_2 , and E/p_0 so that CO_4^- will be the only one of the four possible ion species (see Fig. 6) to enter the photodetachment region. Then while photodetachment measurements are being done in one drift tube, mass identification on the ion will be done in another tube. After mass identification and the establishment of the relative photodetachment cross section of CO_4^- , the relative measurement will be put on absolute scale by calibration against O^- . Finally a sun-light photodetachment rate of CO_4^- will be calculated.

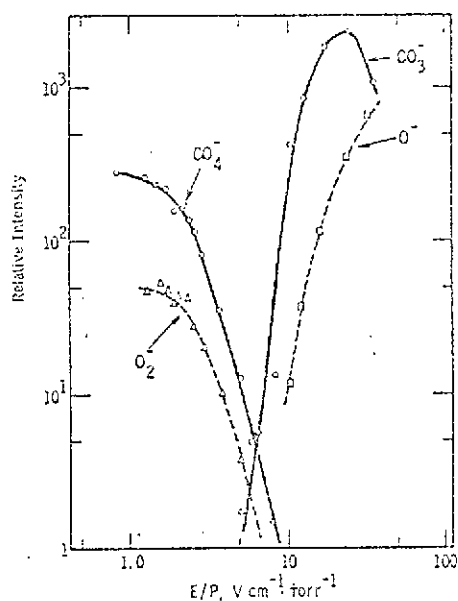


Fig. 6. The relative intensity of various ions found in $O_2 - CO_2$ mixtures as a function of E/p . At low energies O_2^- is initially produced in a 3-body attachment process ($e + O_2 + M \rightarrow O_2^- + M$) and then undergoes 3-body conversion reaction ($O_2^- + CO_2 + M \rightarrow CO_4^- + M$) to produce CO_4^- . At higher energies O^- is initially formed by a dissociative- attachment process and is converted in another 3-body reaction to CO_3^- .
 $P_{CO_2} = 0.8$ torr $P_{O_2} = 0.5$ torr.

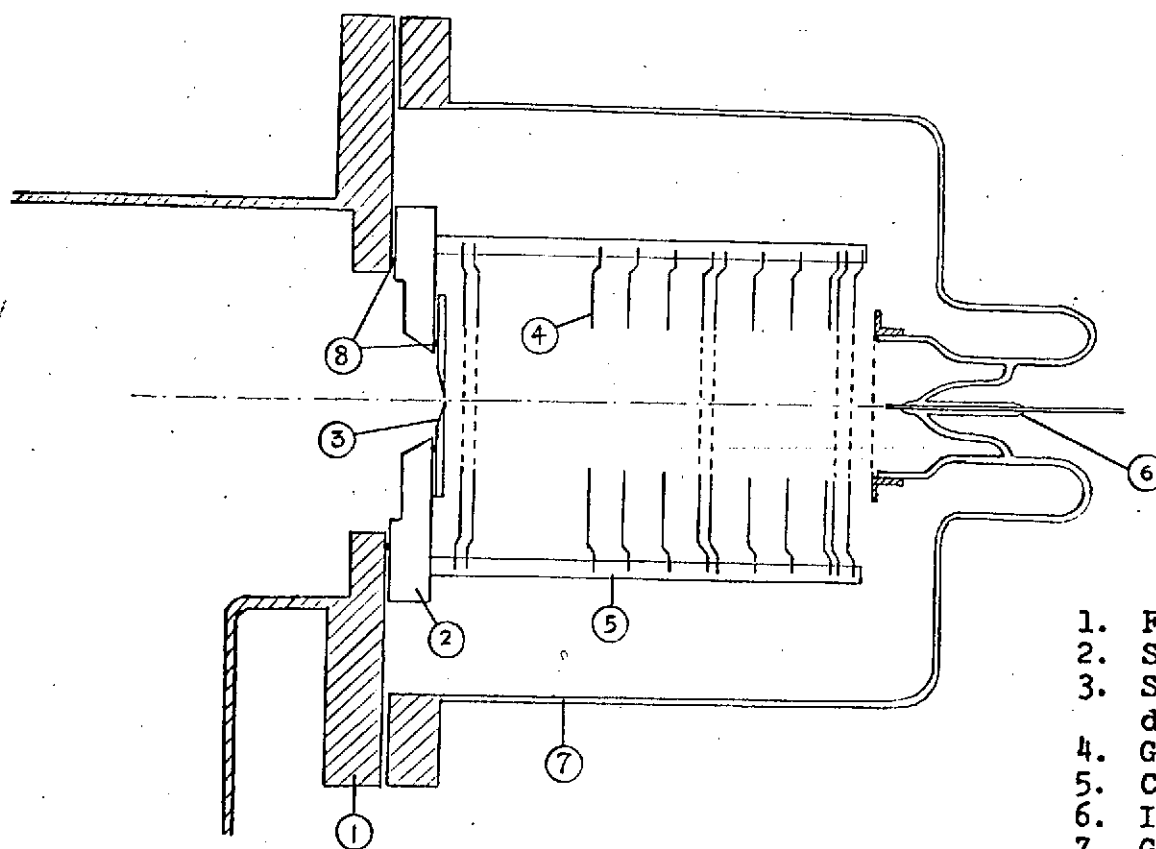
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APPENDIX

Diagrams showing the design
specifications of various components.



1. Flange of T-Assembly
2. Supermica Plate
3. Stainless steel plate with center hole of diameter 0.01".
4. Guard rings
5. Ceramic spacers
6. Ion source
7. Glass to metal adapter (glass ID=6").
8. Gold O-rings

Figure A Drift Tube Assembly

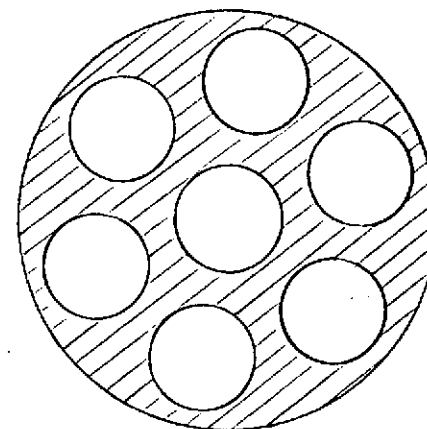
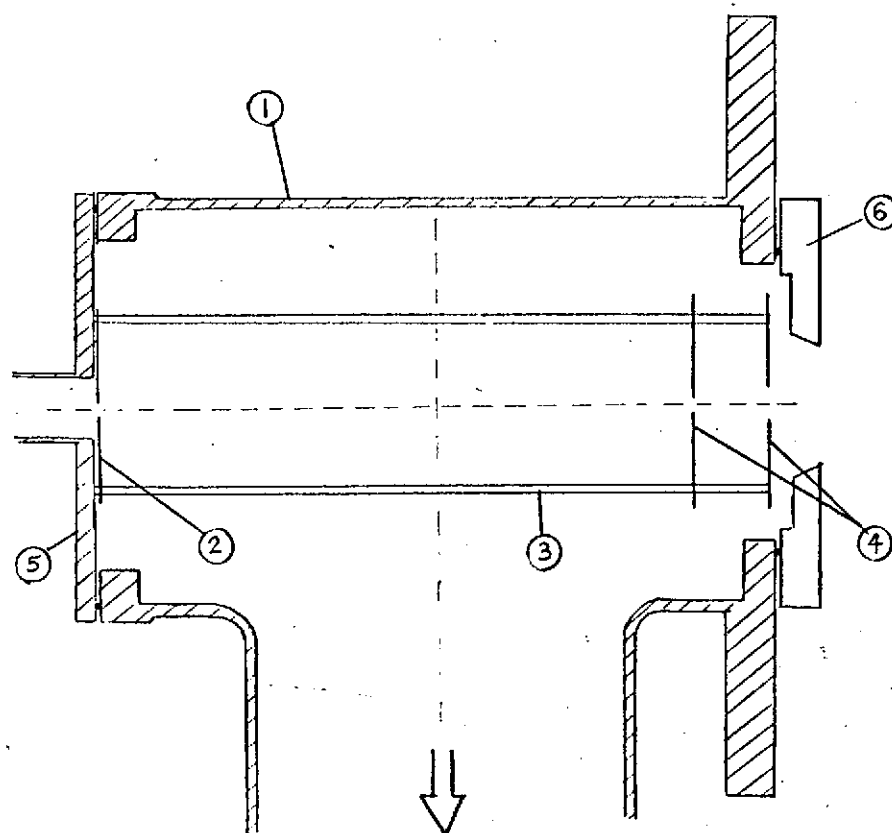


Figure C The Ion Optics Assembly

1. Tee assembly
2. Object slit
3. Stainless steel rod
4. Stainless steel plate
5. Mass spectrometer tube flange
6. Supermica plate.

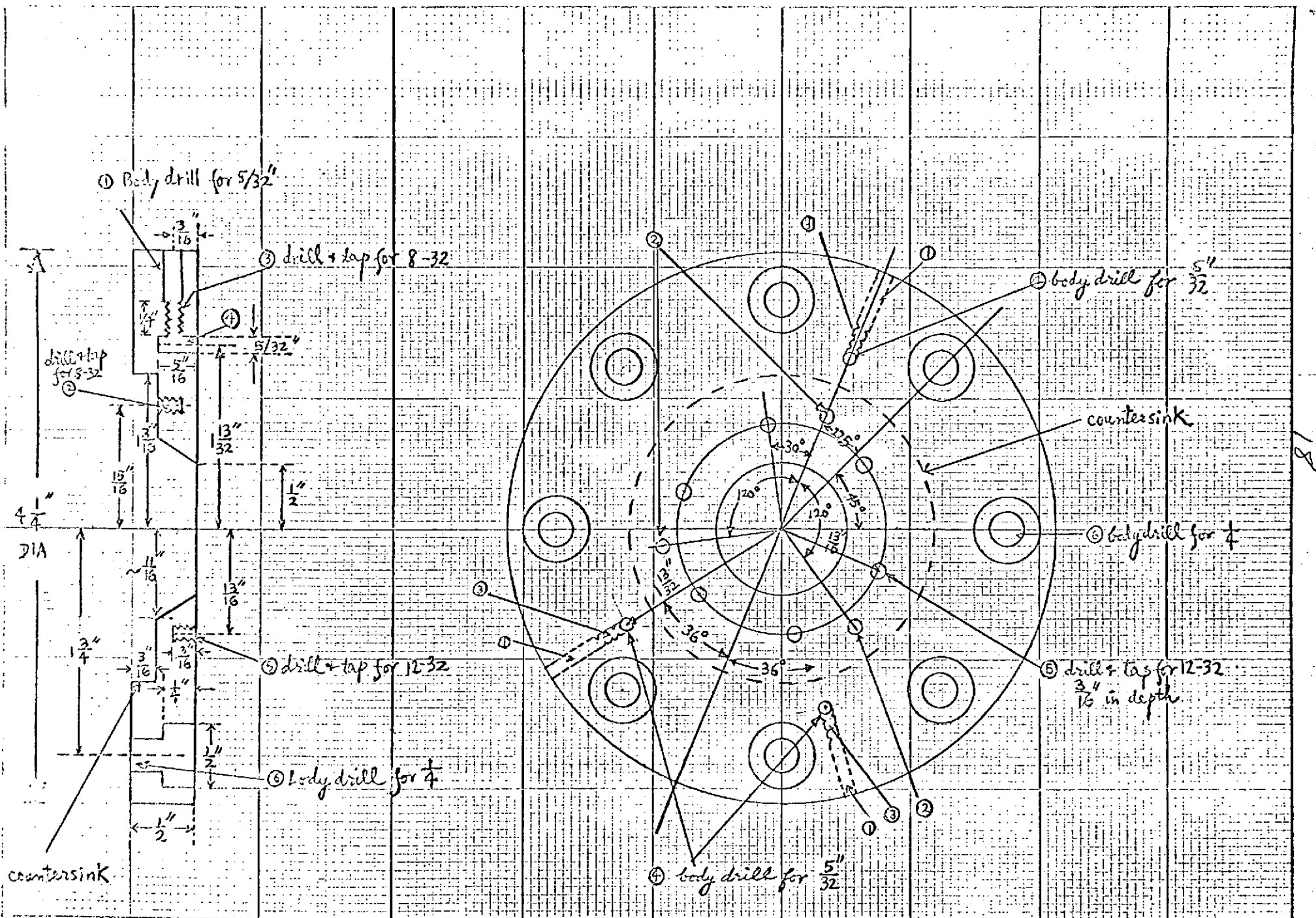


Figure D The Supermica Plate